

# Studies on Photodegradation of Chlorimuron-Ethyl in Soil

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**Abstract:** Photolysis of chlorimuron-ethyl was studied on a soil surface under sunlight and UV light. Eight photoproducts were isolated and characterised by spectroscopic methods. Major photoproducts are formed by cleavage of the sulfonylurea bridge and minor products are formed *via* dechlorination, hydrolysis and cyclisation. The rates of photodegradation of chlorimuron-ethyl on different soils followed first-order rate kinetics, with half lives of 22.3 h, 9.4 h, 4.9 h (UV) and 20.7 days, 11.1 days and 11.1 days (sunlight) for alluvial, red and laterite soils, respectively. The differences in rates of photodegradation were dependent upon the soil pH.

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## 1 INTRODUCTION

Chlorimuron-ethyl, ethyl 2-(4-chloro-6-methoxy-pyrimidin-2-yl-carbamoylsulfamoyl)benzoate, is a sulfonylurea herbicide used for weed control in soybean.<sup>1,2</sup> Like other sulfonylurea herbicides, the primary mode of action of chlorimuron-ethyl involves the inhibition of acetolactate synthase (ALS). Chlorimuron-ethyl is metabolised at a much more rapid rate in tolerant soybean than in susceptible cocklebur (*Xanthium strumarium* L.) or pigweed (*Amaranthus retroflexus* L.). Two products of chlorimuron-ethyl metabolism in soybean have previously been identified: the free acid formed by hydrolysis of the ester and the homogluthathione conjugates formed by displacement of the chlorine atom.<sup>3</sup> Chlorimuron-ethyl degradation in soil occurs primarily by acid-catalysed hydrolysis,<sup>4</sup> and the half-life increases several-fold as the pH increases from 5.0 to 8.0. Chlorimuron mobility and adsorption do not appear to be correlated to any soil type.<sup>5</sup> Chlorimuron adsorption in the Hiwassee loam was attributed to the high hematite and gibbsite content of the soil.<sup>5</sup> Several reports have indicated that chlorimuron-ethyl may persist excessively

under certain environmental conditions and cause injury to non-target plants.<sup>4</sup> This paper provides the first detailed report on the photolysis of chlorimuron-ethyl on soil surfaces under UV light and sunlight.

## 2 MATERIALS AND METHODS

### 2.1 Materials

Technical grade chlorimuron-ethyl (Du Pont East Inc., New Delhi, India) was purified to analytical grade (99.8% purity) by column chromatography on silica-gel. Petroleum ether + acetone eluates (95 + 5 by volume) were collected, evaporated and the residue crystallised from benzene-hexane. The purity was confirmed by thin-layer chromatography and high-performance liquid chromatography (HPLC).

Laboratory grade reagents and solvents locally procured were purified and distilled before use.

### 2.2 Soil characteristics

Alluvial, laterite and red soils were used in the experiment. Their properties are given in Table 1.

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**TABLE 1**  
Physicochemical Properties of Different Soils

Soil	pH	EC <sup>a</sup> (dS m <sup>-1</sup> )	CEC <sup>b</sup> (cmol (P <sup>+</sup> ) kg <sup>-1</sup> )	Clay (%)	Organic carbon (%)
Alluvial	8.1	0.33	10	25	0.68
Red	7.4	0.27	8	10	0.41
Laterite	6.1	0.15	5	12	0.38

<sup>a</sup> EC: Electrical conductivity.

<sup>b</sup> CEC: Cation exchange capacity.

## 2.3 Analytical equipment

### 2.3.1 High performance liquid chromatography

HPLC was carried out with a Waters Assoc. HPLC instrument, Model 40C equipped with a pump (Model 501), a UV detector set at 240 nm and coupled to a printer plotter type recorder. The column used was a 7  $\mu$ m Bondapak reversed phase column (C<sub>18</sub>, 3.9  $\times$  300 mm); mobile phase was methanol + water (6 + 4, by volume) at a flow rate of 1.0 ml min<sup>-1</sup>; volume injected was 20  $\mu$ l.

### 2.3.2 Mass spectrometry

Mass spectra were recorded on a JEOL-JMS-D-300 mass spectrometer using electron impact (EI, 70 eV, direct insertion) with acetone as the solvent. GC-MS were recorded on a Shimadzu QP-2000 instrument (70 eV). The GC conditions were as follows: an ULBORN HR-1 equivalent to OV-1, fused silica capillary (0.25 mm  $\times$  50 m, with film thickness 0.25  $\mu$ m; temperature programme 100°C for 6 min then to 250°C, at 10°C min<sup>-1</sup>).

### 2.3.3 Nuclear magnetic resonance (NMR)

[<sup>1</sup>H]NMR spectra were recorded on a Bruker 400 AC instrument (400 MHz) using tetramethylsilane as an internal standard in deuteriochloroform and recorded as  $\delta$ .

### 2.3.4 UV-Visible spectra

UV-Visible spectra of chlorimuron-ethyl were recorded with a Hitachi Model V-2000 double-beamed UV-VIS spectrophotometer in methanol using a quartz cuvette (1 cm path length).

### 2.3.5 Thin layer chromatography

TLC was performed on a 20  $\times$  20 cm glass plates coated with 0.5 mm silica-gel G, using hexane + acetone (9 + 1 by volume) as developing solvent and iodine as chromogenic reagent.

### 2.3.6 Column chromatography

This was conducted using silica-gel (60–120 mesh) and a 1.5 m chromatographic column with an inside diameter of 2.5 cm. The column was packed using a slurry of silica-gel in petroleum ether.

## 2.4 Photolysis of chlorimuron-ethyl on soil surface

The photolytic degradation of chlorimuron-ethyl on alluvial soil was examined under UV light and sunlight.

### 2.4.1 Preparation of soil thin-layer plates

Soil thin-layer plates were prepared from soil sieved to 2 mm. Each plate contained approximately 20 g of soil applied at a thickness of 2 mm and air-dried before use. Then 10 ml of 100 mg litre<sup>-1</sup> chlorimuron-ethyl was sprayed uniformly over each plate. Ten such plates were prepared. These plates were air-dried and exposed to UV light for 48 h or sunlight for 15 days. The UV light was supplied by a 15-W UV lamp held 30 cm from the test substrate. The light produced by these lamps was rich in irradiation at wavelength 254 nm. Tests with sunlight were run on cloudless April and May days between 9 a.m. and 5 p.m. (8 h per day) on an area of a roof protected as much as possible from the wind. The temperature varied at the test surface between 30 and 35°C in the sunlight and between 25 and 30°C under ultraviolet light. Sunlight intensities at wavelengths between 300 and 400 nm were approximately 720, 780 and 350 mW cm<sup>-2</sup> at the beginning, middle and end of the day respectively. Soil was scraped from the plates and extracted with acetone (3  $\times$  50 ml), mechanically stirred for 1 h followed by centrifugation at 2500 rev min<sup>-1</sup> for 20 min and the supernatant was removed. The same soil was extracted again with methanol (3  $\times$  50 ml) followed by centrifugation and the supernatant was removed. The extracts were combined and concentrated. Photoproducts were separated by column chromatography and identified by spectroscopy.

## 2.5 Rate of photodegradation of chlorimuron-ethyl on soil surface

Three different types of soils (alluvial, laterite and red) were sieved through a 2 mm sieve. Soil thin-layer plates were prepared from a slurry of 1 g of soil in 1 ml of water (1 mm thickness). Sixty plates were prepared to meet the requirement of the experiment. These thin films of soil were uniformly treated with 1 ml of 10 mg litre<sup>-1</sup> solution of chlorimuron-ethyl. Separate plates

were exposed to sunlight or to UV light. The non-irradiated samples were shielded from light by covering with aluminium foil. Soil samples were taken at 1, 3, 6, 9, 12, 15 and 24 h from the plates exposed to UV light and at 5, 10, 15, 20, 25 and 30 days from those under sunlight. At each sampling point, three soil-coated plates were removed and soil was scraped into centrifuge tubes (50 ml). The soil was extracted two or three times with 30 ml acetone by shaker (12 h) followed by centrifuging at  $2500 \text{ rev min}^{-1}$ . Supernatants were decanted and triplicate aliquots of the pooled extracts were concentrated and analysed quantitatively by HPLC.

### 3 RESULTS

#### 3.1 Isolation and identification of photoproducts

Chlorimuron-ethyl, when photo-irradiated under UV light on a soil surface, gave eight photoproducts (2–9) (Fig. 1), whereas under sunlight only photoproducts 2, 3, 6, 8 and 9 were detected. These were separated by column chromatography and purified by preparative TLC. Photoproducts 2, 3 and 8 were major and 4, 5, 6, 7 and 9 were minor.

On the basis of IR,  $^1\text{H}$ NMR and MS the following structures are reported for the photoproducts:

##### 2-Amino-6-chloro-4-methoxypyrimidine (2)

IR:  $\nu$  max  $3460, 3323 \text{ cm}^{-1}$  ( $\text{NH}_2$ ).

$^1\text{H}$ NMR:  $\delta$  6.2 (s, 1H), 3.85 (s, 3H).

MS:  $m/z$  159  $\text{M}^+$ , fragment ions 129 ( $\text{M}^+ - 30$ ),  $-\text{OCH}_3$ ), 124 ( $\text{M}^+ - 35$ ,  $-\text{Cl}$ ).

##### Ethyl 2-aminosulfonylbenzoate (3)

IR:  $\nu$  max  $3385, 3278 \text{ cm}^{-1}$  ( $\text{NH}_2$ ),  $1723 \text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ).

$^1\text{H}$ NMR:  $\delta$  8.15 (dd, 2H), 7.85 (dd, 2H), 5.8 (bs, 2H), 4.46 (q, 2H), 1.46 (t, 3H).

MS:  $m/z$  213  $\text{M}^+$ , fragment ions 121, 104.

##### N-(6-Chloro-4-methoxypyrimidin-2-yl)urea (4)

IR:  $\nu$  max  $3376 \text{ cm}^{-1}$  (NH), 3179 and  $2809 \text{ cm}^{-1}$  ( $\text{NH}_2$ ),  $1712 \text{ cm}^{-1}$  ( $\text{C}=\text{O}$ ).

$^1\text{H}$ NMR  $\delta$  6.5 (s, 1H), 4.0 (s, 3H).

MS:  $m/z$  202 ( $\text{M}^+$ ), fragment ions 186 ( $\text{M}^+ - 16$ ,  $-\text{NH}_2$ ), 158 ( $\text{M}^+ - 44$ ,  $\text{NH}_2\text{C}=\text{O}$ ), 127 ( $\text{M}^+ - 75$ ) and 123.

##### 2-Amino-4-methoxypyrimidine (5)

IR:  $\nu$  max  $3325$  and  $3128 \text{ cm}^{-1}$  ( $\text{NH}_2$ ).

$^1\text{H}$ NMR:  $\delta$  6.8 (s, 2H), 4.0 (s, 3H).

MS:  $m/z$  125  $\text{M}^+$ , fragment ions 94 ( $\text{M}^+ - 31$ ,  $-\text{OCH}_3$ ).

##### 2-Amino-6-chloro-4-hydroxypyrimidine (6)

$^1\text{H}$ NMR:  $\delta$  6.8 (s, 1H), 2.8 (bs, 1H).

MS:  $m/z$  145  $\text{M}^+$ , fragment ions 110 ( $\text{M}^+ - 35$ ,  $-\text{Cl}$ ) 86 ( $\text{M}^+ - 59$ ).

##### N-(2-Ethoxycarbonylphenylsulfonyl)urea (7)

$^1\text{H}$ NMR:  $\delta$  8.3, 7.75, 7.5 (m, 4H), 5.3 (bs, 2H), 4.5 (q, 2H), 1.45 (t, 3H).

MS:  $m/z$  273  $\text{MH}^+$ , fragment ions 228 ( $\text{M}^+ - 44$ ,  $-\text{O}=\text{C}\cdot\text{NH}_2$ ), 214 ( $\text{M}^+ - 59$ ,  $-\text{NHCONH}_2$ ).

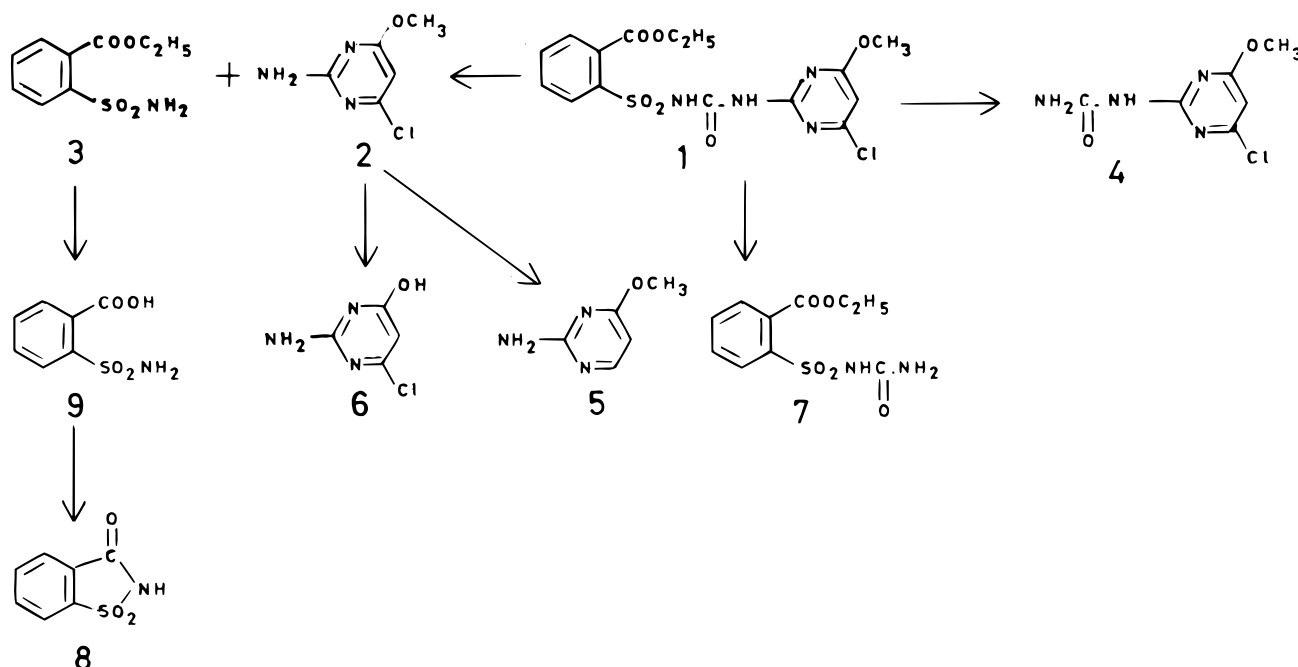


Fig. 1. Possible photoproducts of chlorimuron-ethyl on soil surface.

TABLE 2

Chlorimuron-ethyl Remaining on Different Soils after Exposure to UV Light, Determined by HPLC Analysis

Time (h)	Chlorimuron-ethyl remaining (%) <sup>a</sup>		
	Alluvial soil	Red soil	Laterite soil
0	98.8	98.8	98.3
1	98.5	98.2	82.3
3	87.8	72.3	60.7
5	70.8	69.3	49.9
7	67.4	58.3	39.9
9	62.7	49.5	16.1
15	56.7	37.5	6.6
20	50.4	27.9	—
25	44.3	23.9	—
30	30.5	—	—

<sup>a</sup> Mean of three replicates.

#### *o*-Benzoic sulfimide(saccharin) (8)

MS:  $m/z$  183 ( $M^+$ ), fragment ions 119, 104 and 92.

M.p. (228°C), m.m.p. and mass spectrum identical to that of saccharin, the major soil metabolite of sulfometuron-methyl.<sup>6</sup>

TABLE 3

Chlorimuron-ethyl Remaining in Different Soils after Exposure to Sunlight

Time (days)	Chlorimuron-ethyl remaining (%) <sup>a</sup>		
	Alluvial soil	Red soil	Laterite soil
0	98.8	98.8	98.3
5	98.4	97.7	90.7
10	85.1	72.6	71.3
15	70.3	42.0	38.6
20	59.9	33.6	26.6
25	48.9	27.5	18.7
30	37.9	17.7	15.4

<sup>a</sup> Mean of three replicates.

TABLE 4

Rate Constant ( $K$ ) and Half-Life ( $t_{1/2}$ ) Values for Chlorimuron-ethyl in Different Types of Soil under UV and Sunlight

Soil type	Light	Rate constant ( $K$ )	Half-life	$n^a$	$R^2$
Alluvial	UV	$0.031 \text{ h}^{-1}$	22.3 h	3	0.87
Red	UV	$0.073 \text{ h}^{-1}$	9.4 h	3	0.86
Laterite	UV	$0.140 \text{ h}^{-1}$	4.9 h	3	0.89
Alluvial	Sun	$0.033 \text{ d}^{-1}$	20.7 d	3	0.96
Red	Sun	$0.062 \text{ d}^{-1}$	11.1 d	3	0.92
Laterite	Sun	$0.062 \text{ d}^{-1}$	11.1 d	3	0.87

<sup>a</sup> Number of replicates.

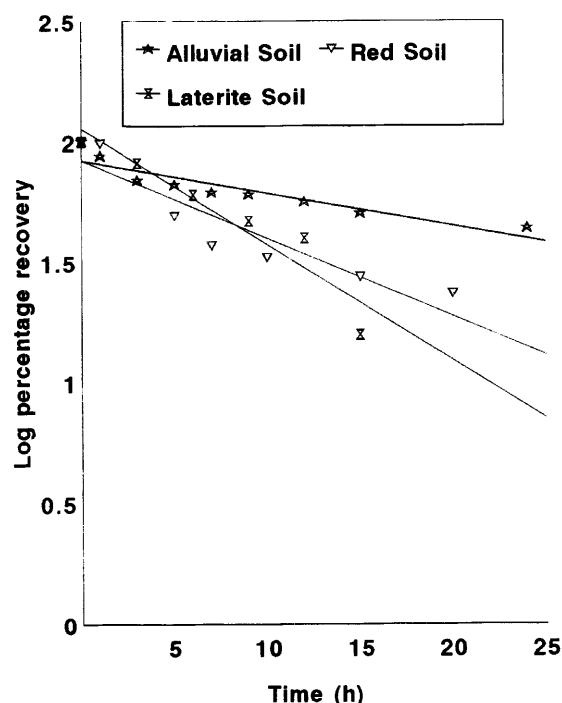


Fig. 2. Linear plot for first-order degradation of chlorimuron-ethyl on soil surface under UV light.

#### 2-Aminosulfonylbenzoic acid (9)

MS:  $m/z$  201 ( $M^+$ ) fragment ions 200 ( $M^+ - 1, H$ ), 77, 55.

### 3.2 Rate of photodegradation of chlorimuron-ethyl on soil surface

The control samples incubated in the dark did not change over the incubation period. This indicates that

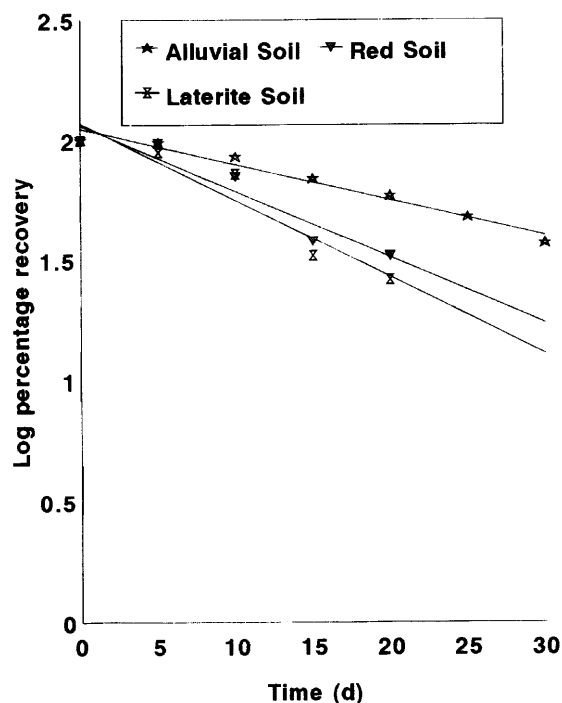


Fig. 3. Linear plot for first-order degradation of chlorimuron-ethyl on soil surface under sunlight.

chlorimuron-ethyl is stable under the conditions and time frame of this study and that the degradation observed in this study can be attributed to photolysis only.

The rate of photodegradation of chlorimuron-ethyl adsorbed on the surface of alluvial, red and laterite soils under UV light and sunlight was studied (Tables 2 and 3). The log percentage concentration of chlorimuron-ethyl, plotted against time, resulted in a straight line (Figs 2 and 3), suggesting first-order rate kinetics with a statistically significant rate constant and high  $R^2$  values (Table 4). The photolysis half lives were (22.26 h, 9.40 h, 4.92 h and 20.69 days, 11.14 days and 11.09 days for alluvial, red and laterite soil under UV and sunlight respectively (Table 4).

#### 4 DISCUSSION

Chlorimuron-ethyl (**1**) absorbs ultraviolet radiation with absorption maxima at 240 and 275 nm. Even at 300 nm (the approximate atmospheric wavelength cut-off for sunlight), it absorbs sufficient energy for the photochemical transformation. Accordingly, adequate absorbance renders chlorimuron-ethyl susceptible to photodegradation by sunlight.

Most of the photoproducts identified from irradiation of chlorimuron-ethyl on a soil surface involved cleavage of the sulfonyl urea bridge (**2** and **3**) and scission of the  $\text{SO}_2\text{NH}$  bond to give **4**. Photoproduct **2** then undergoes dechlorination or demethylation to give photoproducts **5** and **6**, respectively. Photoproduct **3** undergoes hydrolysis to give photoproduct **9**, which cyclises with loss of water to give photoproduct **8** (Fig. 1).

The half-life of **1** was found to be largest on alluvial soil and shortest on laterite soil both under UV light and under sunlight. This suggests that the rate of photodegradation of chlorimuron-ethyl on soil surfaces is affected by soil pH, organic carbon and cation exchanged capacity. The rate of degradation decreases with increase of soil pH and cation exchange capacity as shown in Table 4. The rate of degradation was greater under UV light than under sunlight, suggesting that chlorimuron-ethyl absorbs UV light more strongly at wavelength 270 nm.

#### 5 CONCLUSION

The photochemical fate of chlorimuron-ethyl on a soil surface was investigated. It degraded rapidly on soil with the formation of three major and five minor photoproducts. These products are formed by cleavage of the sulfonylurea bridge, scission of the  $\text{SO}_2\text{NH}$  bond, dechlorination and cyclisation. The rate of degradation on different soils followed first-order kinetics. The results presented in this study clearly indicate the degradation of chlorimuron-ethyl to be dependent upon the soil pH. This study indicates that chlorimuron-ethyl is not very persistent on soil under tropical conditions.

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